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21) International Application Number: PCT/AU 22) International Filing Date: 2 April 1996 30) Priority Data: PN 2187 5 April 1995 (05.04.95)  71) Applicant (for all designated States except US) TRALIAN PETROLEUM PTY. LIMITED Level 14, 167-187 Kent Street, Sydney, NSW 20  72) Inventor; and 75) Inventor/Applicant (for US only): HODGKINSO [AU/AU]; South Street, Lytton, QLD 4178 (AU)  74) Agent: GRIFFITH HACK & CO.; G.P.O. Box 4164 NSW 2001 (AU).	(02.04.9 A ): AU [AU/AU 00 (AU)	CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HO, IS JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, ME MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SE SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian pater (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European pater (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM GA, GN, ML, MR, NE, SN, TD, TG).  Published  With international search report.

#### (54) Title: OIL FOR AGRICULTURAL USE

#### (57) Abstract

An oil for agricultural use having added thereto an oil soluble basic compound or an oil soluble UV deactivator is defined. Preferably the basic compound is: (a) a sulphonate; (b) a phenate; (c) a hydroxy containing compound; and/or (d) an amine. Preferably the UV deactivator is: (a) a UV absorber; and/or (b) a free-radical trap or scavenger.

#### OIL FOR AGRICULTURAL USE

#### FIELD OF THE INVENTION

The present invention relates to an oil agricultural use, in particular to a petroleum derived spray oil "PSO", being primarily an oil for use as an 5 insecticide and/or an acaricidal control spray oil. particularly, the invention relates to a PSO having certain additive(s) which reduces the phytotoxicity of the oil in relation to, for example, crops and plants. The invention will be primarily described in relation to 10 its use with refined and semi-refined light oils, but it should be appreciated that the invention has broader application.

#### BACKGROUND ART

15 Petroleum spray oils ("PSO's") are used agriculture on their own and as carriers or solvents for spraying pesticides, herbicides, micronutrients, chemical adjuvants, etc. The oils are widely used because of their effectiveness in controlling a wide range of pests 20 and diseases, and because of their relatively low cost, relatively low health hazard (including low mammalian toxicity) and wide availability. They also show absence of residual effect against beneficial predators and parisitoids.

However, certain grades and applications of PSO's have been shown to be phytotoxic, particularly in high dosage applications, or in environments where exposure to sunlight is imminent or intense. Acute phytotoxicity can lead to excessive leaf drop in plants and less obvious chronic symptoms such as inhibition of yield of crops.

There has been much debate in the scientific literature as to the mechanisms of oil induced

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phytotoxicity, but a primary source of phytotoxicity has membrane disruption. attributed to disruption involves t he dissolution of folia semipermeable membranes, leading to a breakdown in the plant structure and wilting and/or death of the plant. The problem of membrane disruption was largely overcome by improved oil refinement and the instigation of quality criteria.

Phytotoxic effects have been linked with the distillation temperature or viscosity of the particular oil used in spraying. Phytotoxicity has also been attributed to spray oil dose rate and duration of spraying.

However, photodegradation of modern highly refined PSO's with subsequent phytotoxicity has largely been overlooked by researchers and manufacturers in this area.

The formation of acids in PSO's is associated with the photo-degradation (eg. oxidation) of the PSO mediated by UVA radiation. It is now surmised that a contributing or major factor in the phytotoxicity of PSO's could relate to the level of acidity in the PSO when sprayed, or developed after spraying. Even "superior" spray oils (ie. highly refined spray oils), upon exposure to light, may develop acidity and become markedly phytotoxic. This tendency can be enhanced where an oil applied to a plant is exposed to UV radiation (eg. sunlight) for an extended period of time, so that many of the components of the oil are photo-oxidised into organic acids, in turn attacking the plants.

It would be advantageous if at least preferred embodiments of the present invention provided an oil for agricultural use, in particular an oil for agricultural spraying, that includes therein a component, or components, capable of preventing the formation of acidic products within the oil, or ameliorating or neutralising their effects.

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#### SUMMARY OF THE INVENTION

In a first aspect, the present invention provides an oil for agricultural use having added thereto an oil soluble basic compound.

By employing an oil soluble base, at least some of any acidic compounds present in or formed in the acid can be neutralised.

Preferably, the basic compound is:

- a sulphonate;
- (b) a phenate; 10

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- a hydroxy containing compound; and/or (c)
- (d) an amine.

Thus, a large variety of bases can be added to the oil as appropriate.

In this regard, it is preferred that the basic 15 compound is an overbased sulphonate or phenate, and it is particularly preferred that the basic compound is calcium overbased sulphonate.

Preferably, the calcium overbased sulphonate present in the oil in a range 0.01-5 wt% total. It is most preferred that the calcium overbased sulphonate is present in the oil in an amount of about 1.0 wt% total. A metal overbased sulphonate includes an aqueous micelle defined by a plurality of relatively long-hydrocarbon chain molecules having a polar head (ie. sulphonate functionality) and a hydrophobic tail (eg. long chain alkyl, and an excess amount of metal base, eg. calcium carbonate in the micelle. (A depiction of an overbased sulphonate is shown in Figure 5). Metals other than calcium can also be used in the sulphonate or phenate (eq. magnesium overbased sulphonates).

exposure of а PSO UV described above, As radiation brings about photo-degradation of the PSO (ie. through the photo-oxidation thereof) into peroxides,

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acids, esters, polymers etc, thus increasing the phytotoxicity of the PSO.

In a second aspect, the present invention provides an oil for agricultural use having added thereto an oil soluble UV deactivator.

Photo-oxidation can thus be prevented or ameliorated, or alternatively any photo-oxidation products (eg. peroxide free-radicals) can be scavenged and/or trapped.

Preferably, the UV deactivator is:

a UV absorber; 10 (a)

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a free-radical trap or scavenger. (b)

The UV absorber absorbs UV radiation and thus tends to prevent photo-oxidation, whereas the free-radical trap or scavenger neutralises any free-radicals produced during photo-oxidation (eg. peroxides).

Preferably, the UV absorber is:

- (i) a benzotriazole compound;
- ortho-hydroxy benzophenone compound; (i) or
- benzoxazole, benztriazole (iii) or 20 benzthiazole compound.

In this regard, the UV absorber is preferably TINUVIN 171, pref. at 0.005%. (Trade mark of Ciba Geigy).

Alternatively, the UV absorber can be iso-octyl-3-25 (3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl) (A commercially available form of this propionate. compound is known as TINUVIN 384 (Trade Mark of Ciba Geigy Limited. TINUVIN 384 is a liquid UV absorber of hydroxyphenyl benztriazole class. It has 30 thermal stability and permanence.

Preferably, the iso-octyl-3-(3-(2H-benzotriazole-2vl)-5-tert.butyl-4-hydroxyphenyl) propionate is present in the range of 0.001-0.5 wt% total of the oil, most preferably at about 0.01 wt% total of the oil.

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Preferably, the free-radical trap or scavenger is a metal dithiocarbamate. In this regard it is preferred is the metal dithiocarbamate diamyldithiocarbamate.

A preferred oil for use as a PSO is a refined light oil ( $C_{15}$  to  $C_{35}$  length of hydrocarbon chain). particular, it is preferred that the oil portion of the PSO is a  $C_{15}$  to  $C_{35}$  light paraffinic or light naphthenic petroleum derived oil.

Preferably, the light paraffinic or light naphthenic 10 oil is:

- chemically neutralised; (a)
- clay treated; (b)
- solvent refined; (c)
- (d) hydro-treated. 15

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Physical properties of such oils are shown in Tables 2 and 3.

Surfactants are typically added to PSO's to enable the oil to be dispersed in water for subsequent spraying. Typical surfactants include nonionic surfactants. nonionic surfactants can be added in the range of 0.5 wt% to 20 wt%.

In a most preferred spray oil formulation, a refined light oil can include 0.5 - 20 wt% nonionic surfactant, 1.0 wt% calcium overbased sulphonate and 0.005 benztriazole compound. Thus, preferred formulations may include both an oil soluble basic compound and a UV deactivator.

In a further aspect of the present invention an additive composition for an oil for agricultural use is provided which can include a base (as defined above), and/or a UV deactivator (as defined above).

additive composition also include This can emulsifying surfactant(s) (as defined above). additive composition can be provided separately from the oil (eg. PSO) and can be added to the oil in situ (eg.

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prior to spraying). The additive composition finds useful application when added to less than ideally refined oils, or oils that are in various stages of oxidation, and can stabilise, eliminate or reduce the phytotoxicity of such oils prior to spraying etc.

## BRIEF DESCRIPTION OF THE DRAWINGS

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example, and also in conjunction with the attached Figures in which:

Figure 1 shows the effect of acidity on betacyanin efflux and the control thereof by adding calcium overbased sulphonate to oils (with reference to oils without such addition);

Figures 2 and 4 show the effect of adding a base and UV deactivator to different oils when exposed to UV radiation;

Figure 3 shows a fourier transform infra-red carbonyl peak measurement (ie. measurement of acidity) for different oils with base and/or UV deactivator added thereto;

Figure 5 depicts schematically typical molecular structures of sulphonates and phenates;

Figure 6 shows the UV absorption spectra of typical 2-hydroxybenzophenones (as preferred UV deactivators);

Figure 7 shows schematically the molecular structure of TINUVIN 384; and

Figure 8 shows the transmission spectrum for various solution concentrations of TINUVIN 384 in toluene.

#### MODES FOR CARRYING OUT THE INVENTION

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Some non-limiting examples of preferred embodiments of the invention will now be described.

#### EXAMPLES

A standard nomenclature has been employed throughout the examples for the petroleum spray oils. For example, when a PSO is referred to as a 60N or 70N oil, the number portion refers to and is derived from the measurement of viscosity in Saybolt universal seconds and the term neutral (N) refers to the paraffinic nature of the oil.

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When the terminology ASTM and AS is used throughout the specification it is a reference to American Society for Testing and Materials and Australian Standard respectively.

Membrane disruption (and thus phytotoxicity), as referred to in the Figures has been measured by the Betacyanin Efflux Test. The standard test is applied on beetroot tuba disks which have no cuticle and thus the effects of a PSO on the cell membrane can be monitored directly.

# 20 <u>MEMBRANE DISRUPTION BY BETACYANIN EFFLUX FROM UNPROTECTED</u> CELL MEMBRANES

Oil induced disruption of cell membranes unprotected by a cuticle layer was measured by betacyanin efflux from beetroot tuba disks (Coupland, D. et al. (1989) Evaluation of three techniques used to determine surfactant phytotoxicity; Annals of Applied Biology 115, 147-156). Test material was prepared by making 7 mm diameter disks with a cork borer and cutting them to 1 mm thickness. Preliminary studies showed disks were best used after a two hour rinse in tap water followed by air drying. It was essential to remove adsorbed water because water induced premature betacyanin efflux.

Dry disks (n=3) of known fresh weight were added to 10 mL test tubes and completely covered by 2 Ml oil. The

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treatments were then incubated for 3 hours at 30°C when isotonic solution of 5 Ml of 0.4 M sorbitol in The tubes were set aside to deionised water was added. allow betacyanin efflux for 18 hours at 20°C. aqueous layer was performed by colorimetric of analysis at 535 nm in 1 cm cells against a solvent blank. normalised then readings were Absorbance absorbance/disk weight to eliminate differences between This procedure together with the choice of three successful in obtaining was disks randomly chosen reproducible results. Cooking of the disks to produce a maximum efflux for normalisation purposes did not improve the precision.

The pink colour developed by betacyanin efflux conformed to a classical logistic curve when calibrated with oil acidity. The effective dose ( $\mathrm{ED}_{50}$ ) for 3 hours contact was 0.11 mg KOH/g oil (ASTM D927) and the detection limit for no observable effect was 0.08 mg KOH/g oil (0.5 Abs units/g).

In the Figures and Tables, the phytotoxicity of various spray oils, as determined by betacyanin efflux, is shown.

From the tests, it was established that when a membrane disruption value of 0.5 Absorbance Units/g specimen (Abs/g) was exceeded, then damage to the plant would follow. In other words, a result of 0.5 or less is a phyto-safe membrane disruption value.

#### Example 1 (Figure 1)

Various levels of calcium overbased sulphonate, (shown as "base" in Figure 1) were added to 70N and 150N oils, both oxidised and unoxidised. As shown clearly in Figure 1, with the addition of both 0.1% of the base and 1% of the base, the membrane disruption value is held below about 0.4 Abs/g (which is in the phyto-safe zone). Figure 1

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also compares these oils against standard oils of different acid values.

#### Example 2 (Figure 2)

A 70N oil had a number of additives (as shown in Figure 2) added thereto. Figure 2 shows the effects of exposing the oil to 4mW of UV radiation/cm<sup>2</sup> with time, and also indicates the effects of variation in the levels of base (eg. calcium overbased sulphonate) and UV deactivator (eg. TINUVIN 384).

#### 10 Example 3 (Figure 3)

A 70N oil (with similar additives to Example 3) was exposed to 4mW of UV radiation/cm<sup>2</sup>. Figure 3 shows the results from a fourier transform infra-red spectrum of the oil with time, indicating the variation in acidity between various "treated" and "untreated" oils. From Figure 3, it can be seen that the addition of even a small amount of base and UV deactivator minimises the formation of acids (indicated by the carbonyl function, ie. absorbance at 1710 cm-<sup>1</sup>).

## 20 Example 4 (Figure 4)

In a similar manner to Example 2, a 70N oil had a number of additives added thereto and was then exposed to UV radiation. The acidity of the resultant oil with time is shown for various combinations of the base and UV deactivator, indicating that excellent results are obtained when both a base and a UV deactivator are present.

#### Example 5

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Various additive compositions for use as a separate an additive or concentrate pack for addition to oils for agricultural use were prepared. The additive compositions most typically included one or two nonionic

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surfactants (ie. emulsifying surfactants to render the oil suitable for use as a PSO (eg. in water)), and an oil soluble base (eg. calcium overbased sulphonate) and/or a UV deactivator (eg. TINUVIN 384).

An advantage of an additive composition is that it can be added to PSO's in situ (ie. it can be transported in a concentrate form to the user of the PSO, who then adds an appropriate dosage). This means that a local or regional oil can be employed (ie. the treated oil itself does not need to be transported to site) and thus transportation costs can be reduced.

A most preferred additive composition was as follows: Nonionic surfactant(s) plus calcium overbased sulphonate and benztriazole compound in a ratio of 140.5:1, (not including surfactant).

#### Example 6

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Another preferred formulation for a light petroleum spray oil included 0.5 - 20 wt% nonionic surfactant, 1.0 wt% calcium overbased sulphonate and 0.05 wt% TINUVIN 384.

below summarises the photo-degradation 20 Table 1 performance of various compositions when added to 60 Neutral oil, 70 Neutral oil and 150 Neutral oil, against these oils by themselves. This Table demonstrates the broad applicability of the formulation in different types of oil, and shows that membrane disruption and acidity 25 are considerably reduced or eliminated when such additives are present.

Table 2 shows the typical chemical characteristics of petroleum spray oils suitable for use with the present invention. Table 3 shows some of the properties of a broad range of light spray oils suitable for use in the present invention. Table 4 shows absorption spectra of a

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number of different benzophenones for use as a UV deactivator.

#### Figure 5

Figure 5 shows a schematic representation of the typical overbased sulphonates structures of phenates, wherein the micelle is defined by a plurality of water-soluble polar sulphonate functionality groups (hydrophilic heads) facing inwardly, with each sulphonate oil soluble non-polar alkyl head having an (hydrophobic tail) projecting outwardly therefrom. 10 The overbased sulphonates contain an excess amount of metal base (eg. calcium carbonate) which neutralises acids formed during photo-degradation of the oils. The alkyl chain length of the sulphonates ranges from 18 to over 20 carbon atoms, whereas the alkyl chain length of 15 the phenates contains approximately 12 carbon atoms.

#### Figures 6, 7 and 8

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Figure 6 shows the UV absorption spectra of typical 2-hydroxybenzophenones which can be used as a UV deactivator in some forms of the present invention. (Table 4 also shows the absorption spectra of different benzophenones).

Figure 7 shows the chemical structure of TINUVIN 384 and

Figure 8 shows a transmission spectra for various concentrations of TINUVIN in toluene, indicating its preferred usage as a UV absorber.

From the above description, it can be seen that the addition of an oil soluble base and an oil soluble UV deactivator (in various preferred configurations) can eliminate, ameliorate or reduce membrane disruption (as

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measured by betacyanin efflux) and acidity in petroleum spray oils (resulting from the photo-degradation/photo-oxidation of spray oils in the presence of oxygen and UV radiation), thereby reducing the phytotoxicity of spray oils.

The invention finds application with a wide variety of spray oils, and particularly with less than ideally refined base oils. Thus, by adding a preferred composition to such non-ideally refined spray oils, they can immediately be used thereafter with a reduced risk of phytotoxicity.

Whilst the invention has been described with reference to a number of preferred embodiments, it should be appreciated that the invention can be embodied in many other forms.

TABLE

THE EFFECT OF ADDITIVES IN PETROLEUM SPRAY OIL

	<del></del>		<del></del>			
Acidity mg KOH/g	0.26	0.009	0.3	0.007	0.77	0,26
Carbonyl peak (Abs. units)	0_1209	0.0678	0.1421	0.0858	0.2118	0.1395
Betacyanin efflux (Abs/d)	2.45	0	3.16	Ö	2.57	0
Treatment exposed for 20 hours	60 Neutral oil	60 Neutral oil + 1% base +0.005% UV deactivator	70 Neutral oil	70 Neutral oil + 1% base +.005% UV deactivator	150 Neutral oil	150:Neutral:oil + 1% base +0:005% UV deactivator

TABLE 2

TYPICAL CHEMICAL CHARACTERISTICS OF PETROLEUM SPRAY OILS

Analysis	Method	Typical base oil <sup>A</sup>	AS 1888 C21 NR class <sup>B</sup>	AS 1888 C23 NR class <sup>B</sup>
Density @ 15°C	ASTM D1298 (g/mL)	.846	< 0.870	< 0.880
Refractive index @ 20°C	ASTM D1218	1.4680	· -	-
Viscosity @ 40°C	ASTM D2270 (cSt)	12	-	-
%UR	ASTM D483	94	>92	>92
Carbon No. @10% <sup>c</sup>	Furness et al. 1987	20.2	>18.2	>19.0
Carbon No @50%	n	23.5	>21	>22.0
Carbon No. @90%	H	25.3	<24.2	<26.0
50% DT	ASTM D2887	385°C	>357°C	>369°C
50% DT	ASTM D1160	231°C	>206°C	>217°C
Boiling range	ASTM D2887	57°C	<74°C	<81°C
%Cp	ASTM D3238	70	-	-
%Cn	u	28	-	-
%Ca	**	2	-	-
%Aromatic mass	ASTM D2549	10	_	-

A = 70 Neutral

B = Proposed Australian standard [Furness et al. 1987]. These classes equate to the USA "superior " oil grade.

C = Carbon Number when X% mass has distilled.

NR = Narrow Range

%Cp = % carbon atoms as paraffin, n = naphthene, a = aromatic

DT = Distillation temperature (C°: @ 101 kPa ASTM D2887 or 10 kPa ASTM D1160).

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CAS name of	CAS No.	Carbon number distribution	Remarks
Chemically neutralized light paraffinic	64742-28-5	C15-C30	Contains relatively large proportion of saturates
Chemically neutralized light naphthenic	64742-35-4	·C15-C30	Few normal paraffins
Clay treated light paraffinic	64742-37-6	C15-C30	Mostly saturates
Clay treated light naphthenic	64742-45-6	C15-C30	Few normal paraffins
Solvent refined light paraffinic	64741-89-5	C15-C30	Predominantly saturates
Solvent refined light	64741-97-5	C15-C30	Few normal paraffins
Hydrotreated light paraffinic	64742-55-8	C15-C30	Contains a relatively large proportion of saturates
Hydrotreated light naphthenic	64742-53-6	C15-C30	Few normal paraffins

A: US EPA (1978); TSCA, US Toxic substances control act.

B: CAS number: Chemical abstracts service registry number.

TABLE 4

ABSORPTION SPECTRA OF BENZOPHENONES

Damanahamana	a		. Ъ		E		D.f
Benzophenone (suostiluents)	1 max	log Б	l max	log E	λ maz	log e	Ref.
None	250	4.30			333	r.85	89
4-OH	2 <u>4</u> 8	4.00	289	<u> </u>			II-
4-0H 4.4'-di-0H		·	<b>29</b> 5	4.28			114
4.4 -CH 2-OH	251	4-04		· <del></del>	342	3.20	89
z-OMe	25I	404			347	3.20	89
2-OME 3-OME	<b>2</b> 56	4.05					89
3-0Me 2,4-di-OH	212	3-94	290	3-96	338	4.I2	II4
2,6-di-OH	250	4.07	28°C	3-74			II4
2,6-di-OH5-∳CO	248 248	4.30	290	3-90	3 <u>1</u> 8	4-34	I I -
2,4-di-OH—5-¢CO	258	<del>4</del> -27	2 <sub>75</sub>	4.26	338	4.15	II4
2,6-di-OH-3,5-di-9CO	258	4.30	280	4.53	330	3.91	II
2,4-di-OH-4'-OMe	2 <u>5</u> 6	<u>4 ~ 6</u>	285	4.29	325	414	IL
2,4-di-OH4'-Me	250	3-93	290	407	340	<u>+</u> 09	II
2,4-di-OH4'-CI	250	8َهُـهِ	290	02 ــــــــــــــــــــــــــــــــــــ	325	404	II4
2,4-di-OH-3',4'-di-Cl	252	ġ.98	290	4.10	325	3.96	II4
2,4-di-OH—2',4'-di-OH	242	3.80	283	3-9¢	352	4.17	II4
2,4-di-OMe	242	814	280	3.86	310	3-78	II4
2,4-(11-OME 2-OH—4-OME	_ <del></del>		289	4.13	322	3.96	ΙΙ
2-OH-4-OME			285́	<u>+</u> 20	320	4.12	II
2-OH-4,4'-di-OMe 2-OH-4-OMc-3-Me	250	3.8g	зоŏ	4.27			ΙΙ

#### CLAIMS:

1. An oil for agricultural use having added thereto an oil soluble basic compound.

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- 2. An oil as claimed in claim 1, wherein the basic compound is:
  - (a) a sulphonate;
  - (b) a phenate;
  - (c) a hydroxy containing compound; and/or
  - (d) an amine.
- 3. An oil as claimed in claim 2, wherein the basic compound is an overbased sulphonate or phenate.
  - 4. An oil as claimed in claim 2 or claim 3, wherein the basic compound is a calcium overbased sulphonate.
- 5. An oil as claimed in claim 4, wherein the calcium overbased sulphonate is present in the oil in a range 0.01-5.0 wt% total.
  - 6. An oil as claimed in claim 5, wherein the calcium overbased sulphonate is present in the oil in an amount of about 1.0 wt% total.
- 7. An oil for agricultural use having added thereto an oil soluble UV deactivator.
  - 8. An oil as claimed in claim 7, wherein the UV deactivator is:
    - (a) a UV absorber;
- 25 (b) a free-radical trap or scavenger.
  - 9. An oil as claimed in claim 8, wherein the UV absorber is:

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- a benzotriazole compound;
- (ii) an ortho-hydroxy benzophenone compound;
  or
- (iii) a benzoxazole, benztriazole or benzthiazole compound.
  - 10. An oil as claimed in claim 9, wherein in (i) the UV absorber is:
  - (a) TINUVIN 171; or
- (b) iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-10 4-hydroxyphenyl) propionate.
  - 11. An oil as claimed in claim 10, wherein compound (b) is present in the range of 0.001-0.5 wt% total.
- 12. An oil as claimed in claim 10, wherein compound (a) is present at about 0.005 wt% total; or compound (b) is present at about 0.1 wt% total.
  - 13. An oil as claimed in claim 8, wherein the free-radical trap or scavenger is a metal dithiocarbamate.
  - 14. An oil as claimed in claim 13, wherein the metal dithiocarbamate is zinc diamyldithiocarbamate.
- 20 15. An oil as claimed in any one of the preceding claims, wherein the oil portion is a  $C_{15}$  to  $C_{35}$  light paraffinic or light naphthenic petroleum derived oil.
  - 16. An oil as claimed in claim 15, wherein the light paraffinic or light naphthenic oil is:
    - (a) chemically neutralised;
    - (b) clay treated;

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- (c) solvent refined; or
- (d) hydro-treated.

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- 17. An oil as claimed in any one of the preceding claims, further including emulsifying surfactant(s).
- 18. An oil as claimed in claim 17, wherein the surfactant(s) is/are nonionic surfactant(s) and is/are added at about 0.5 wt% to 20.0 wt% total of the oil.

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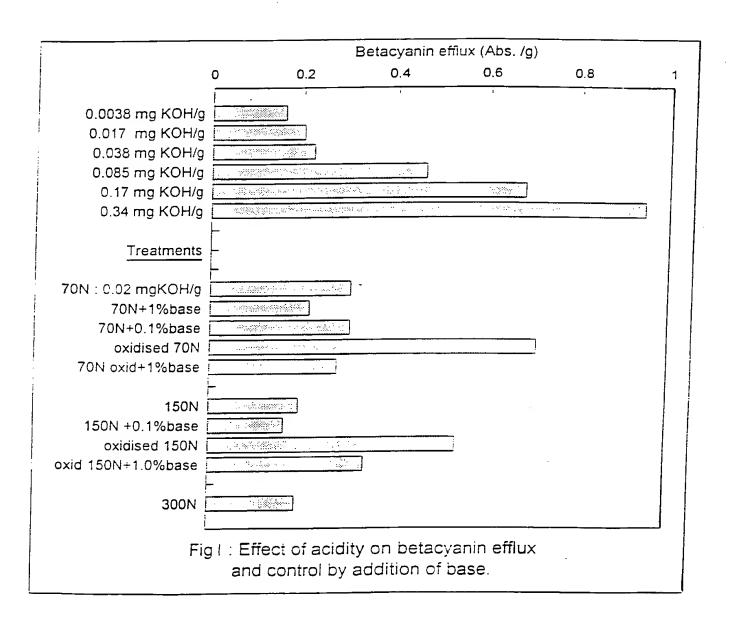
- 19. An oil for agricultural use including the oil soluble basic compound as defined in any one of claims 1 to 6 and the UV deactivator as defined in any one of claims 7 to 14.
- 10 20. An additive composition for an oil for agricultural use including a base as defined in any one of claims 1 to 6 and/or a UV deactivator as defined in any one of claims 7 to 14.
- 21. An additive composition as claimed in claim 21, wherein the oil to which the composition is added is as defined in claim 15 or claim 16, and wherein the additive composition optionally includes emulsifying surfactant(s) as defined in claim 17 or claim 18.

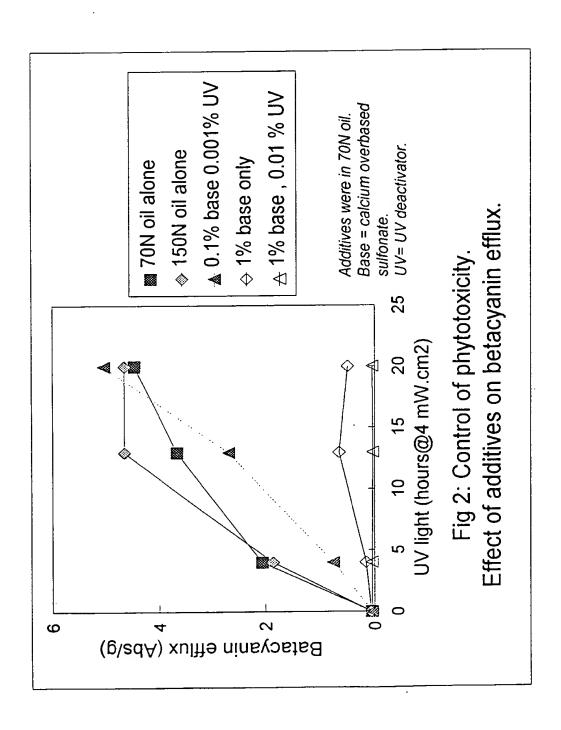
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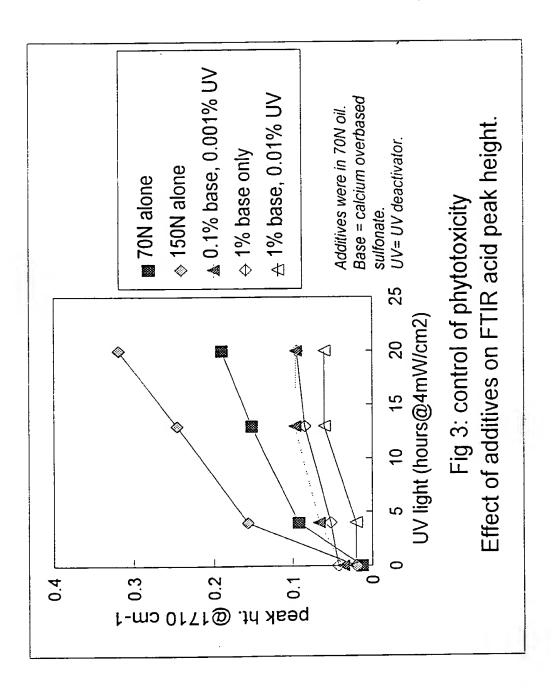
AUSTRALIAN PETROLEUM PTY LIMITED

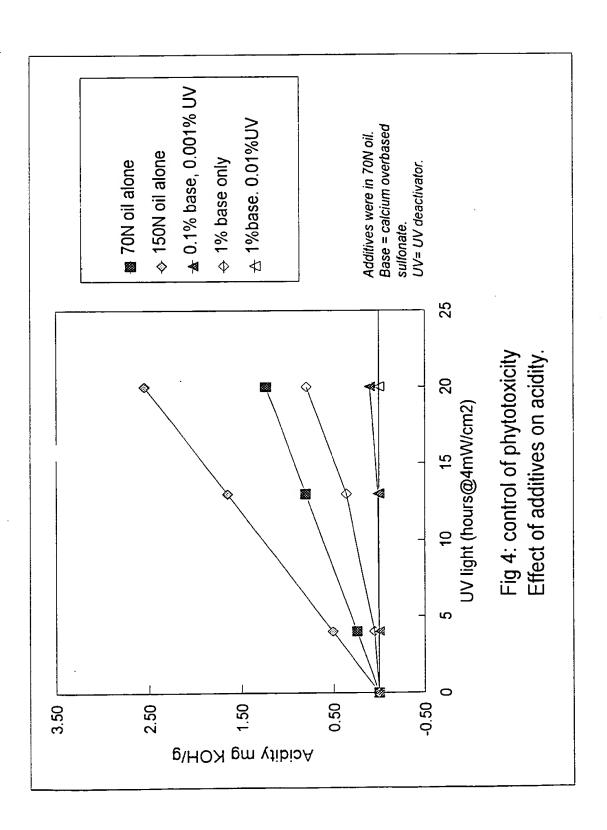
By their Patent Attorneys

GRIFFITH HACK & CO.



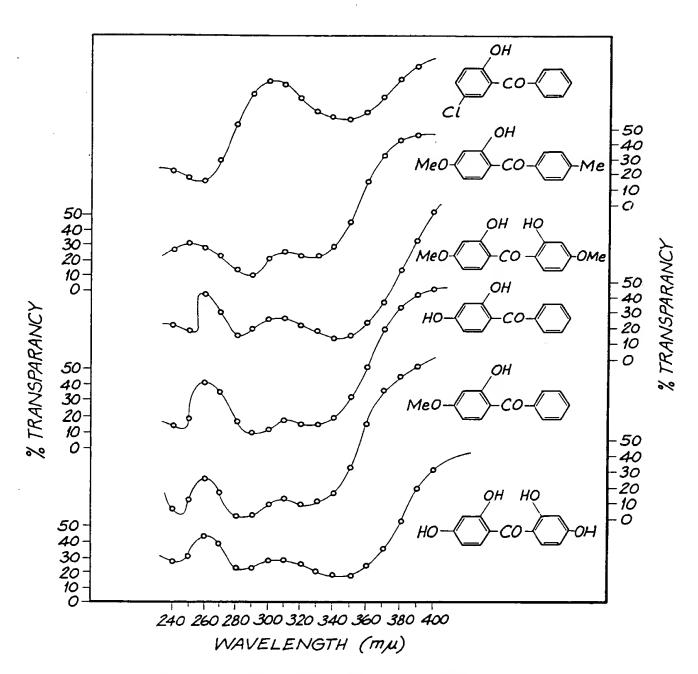






5/7

FIG. 5



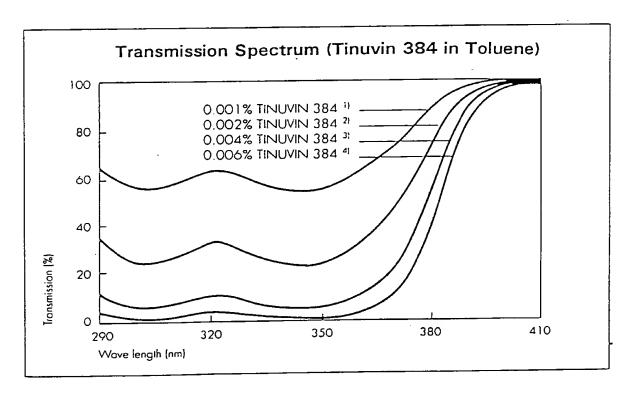
U.V. ABSORPTION SPECTRA OF TYPICAL
2-HYDROXYBENZOPHENONES

# FIG. 6

#### **FIGURE**

Iso-octyl-3-(3-(2H-benzotriazol-2-yl)-5-tert. butyl-4-hydroxyphenyl)propionate Molecular weight: 451.6

FIGURE 8



Absorption maximum: 343 nm

 $^{11}$  corresponds to 0.25 % in a 40  $\mu m$  film  $^{21}$  corresponds to 0.5 % in a 40  $\mu m$  film

 $^{31}$  corresponds to 1.0% in a 40  $\mu m$  film

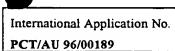
4) corresponds to 1.5% in a 40 µm film



International Application No.

			PCT/AU 96/00189			
A.	CLASSIFICATION OF SUBJECT MATTER					
Int Cl <sup>6</sup> : A0	IN 25/02, 25/22, 25/32					
According to	International Patent Classification (IPC) or to bot	h national classification and	IPC			
	FIELDS SEARCHED					
	mentation searched (classification system followed by 65/02, 25/22, 25/32, A61K 7/42, 7/44	classification symbols)				
	searched other than minimum documentation to the ex N 25/02, 25/22, 25/32	tent that such documents are in	cluded in the fields searched			
FILE WPAT	base consulted during the international search (name of calcium(5w) sulphonate, tinuvin, oil, agriculated ABSTRACTS: uv or ultraviolet, calcium	tur:, phytotoxic:, uv or ultr	raviolet, A01N, A61K			
C.	DOCUMENTS CONSIDERED TO BE RELEVAN	Г				
Category*	Citation of document, with indication, where ap	propriate, of the relevant pas	ssages Relevant to claim No.			
х	US 3565599 (KAMIL M. SOR et al) 23 Februar entire document, especially column 3 lines 34-3		1, 2, 15			
x	DE 2753183 A1 (REANAL EINOMVEGYSZERGYAR) 27 July 1978 example 1 page 24, example 6 page 26, example 9 page 27  1, 2, 20					
x	US 3504091 (S. H. J. AKERSTROM et al) 31 M column 2 lines 31-37	March 1970	20			
x	Further documents are listed in the continuation of Box C	X See patent famil	y annex			
* Special categories of cited documents:  "A" document defining the general state of the art which is not considered to be of particular relevance  "E" earlier document but published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means  "P" document defining the general state of the art which is not considered to be of particular relevance and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the						
Date of the actu	al completion of the international search	Date of mailing of the interna	10.00			
3 June 1996			NE 1996.			
Name and mails AUSTRALIAN PO BOX 200 WODEN ACT AUSTRALIA	ing address of the ISA/AU INDUSTRIAL PROPERTY ORGANISATION 2606 Facsimile No.: (06) 285 3929	MARK ROSS Telephone No.: (06) 283 2281	and XIX			





	Citation of document with indication where appropriate of the relevant passages	Relevant to
Category*	Citation of document, with indication, where appropriate, of the relevant passages	claim No.
	EP 456198 A1 (HODOGAYA CHEMICAL CO. LTD. AND TOHO CHEMICAL INDUSTRY	
	CO. LTD.) 13 November 1991	
X	page 3 line 12 and page 3 lines 21-25	20
	Derwent Abstract Accession No. 78671 D/43, Class C03, JP,A, 56-115739 (KURARAY KK)	
	11 September 1981	
X	abstract	7,8
Y		9-16
	US 4125400 (J. D. DOWNER, C. A. L. PHILLIPS), 14 November 1978	
X	entire document, especially column 2 lines 28-30	1, 2, 15
Y		2-21
	EP 225580 A2 (AMOCO CORPORATION), 16 June 1987	
X	entire document, especially page 1 lines 32-33	20
Y		1-6, 15-18, 2
	EP 312313 A1 (EXXON CHEMICAL PATENTS INC.) 19 April 1989	
X	entire document	20
Y		1-6, 15-18, 2
	US 3377281 (H. D. GOWER) 9 April 1968	
X	entire document	20 1-6, 15-18, 2
Y		1-0, 13-18, 2
	US 5439602 (A. D. ECKARD, I. RIFF) 8 August 1995	20
PX	entire document	20
PY		1-0, 13-10, 2
	DE 4318210 A1 (CHEMBICO) 8 December 1994	7 10 20 2
<b>, Y</b>	entire document	7-18, 20, 2
	THE ALCOHOL OF THE CRAIM OF THE PARTY OF THE	
A	US 4165230 (R. E. GRAVROK, C. A. L. PHILLIPS) 21 August 1979 entire document	1-21
Α	entire document	
	US 4665059 (T. TOZAWA, M. ENDO) 12 May 1987	
Α	entire document	1-21
••		
	AU,A, 16006/88 (F. C. GASKIN) 16 November 1989	
Α	entire document	7,8
	AU,A, 22433/88 (L'OREAL) 23 March 1989	
Α	entire document	7, 8
		1



International Application No. PCT/AU 96/00189

# Information on patent family members

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Doo	rument Cited in Search Report			Patent	Family Member		
DE	2753183 Al	DK	5063/77	IN	147099	YU	2745/77
EP	456198 A1	CN	1056216	JP	4018002		
EP	225580 A2	AU	65531/86	CA	1283093	JP	62181397
		US	4664822	US	4767551		
EP	312313 A1	BR	8805248	CN	1034752	EP	312315
		GB	8723907	US	5089155	US	5112506
		US	5137648	JP	1174597	JP	2084493
		SG	910/94	SU	1838391	BR	8805249
US	4665059	JP	59122408	US	4541859		
AU	16006/88	US	4806344	US	5006331	US	5256403
AU	22433/88	AT	2278/88	BE	1002094	CA	1307468
		СН	677603	DE	3831920	FR	2620618
		GB	8822053	GB	2209941	GB	88100620
		IT	8867836	IT	1223839	. JP	1106814

# TENT COOPERATION TREATY PCT

EC'D	2	5	MAR	1997,
WIPO		Ρ	СТ	

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P05319-EI/RPW:SLC	FOR FURTHER ACTION		f Transmittal of International Preliminary ort (Form PCT/IPEA/416).	
International application No.	International filing da	ate	Priority Date	
PCT/AU 96/00189	2 April 1996	·	5 April 1995	
International Patent Classification (IPC)	or national classificat	ion and IPC		
Int. Cl. <sup>6</sup> A01N 25/02, 25/22, 25/32				
Applicant (1) AUSTRALIAN PETROLE (2) HODGKINSON, Mark	EUM PTY LIMITED	)		
This international preliminary     Authority and is transmitted to			nis International Preliminary Examining	
2. This REPORT consists of a to				
X This report is also accome been amended and are the (see Rule 70.16 and Section 1).	ne basis for this report	and/or sheets contain	scription, claims and/or drawings which have ing rectifications made before this Authority under the PCT).	
These annexes consist of a total	al of 6 sheet(s).			
3. This report contains indications relat	ing to the following ite	ems:		
I X Basis of the repor	1			
II Priority				
III Non-establishmer	nt of opinion with rega	ard to novelty, inventi-	ve step and industrial applicability	
IV X Lack of unity of i	nvention			
	ent under Article 35(2) lanations supporting su		y, inventive step or industrial applicability;	
VI X Certain document	ts cited			
VII Certain defects in	the international appl	lication	1 1 1	
VIII X Certain observation	ons on the internationa	al application		
Date of submission of the demand 30 October 1996		Date of completion of the report 6 March 1997		
Name and mailing address of the IPEA AUSTRALIAN INDUSTRIAL PROPERTY PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. (06) 285 3929	ORGANISATION	J. BODEGRAVEN Telephone No. (06) 2		

IV.	Lack of unity of invention
1.	In response to the invitation to restrict or pay additional fees the applicant has:
	restricted the claims.
	paid additional fees.
	paid additional fees under protest.
	neither restricted nor paid additional fees.
2.	This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3.	This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is
	X complied with.
	not complied with for the following reasons:
4.	Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:
	X all parts.
	the parts relating to claims Nos.

<b>V</b> .	Reasoned statement under Ar citations and explanations sup	e step or industrial applicability;	
1.	Statement		
	Novelty (N)	Claims 6-14	YES
		Claims 1-5,15-16	NO
	Inventive step (IS)	Claims 6-14	YES
	• • •	Claims 1-5,15-16	NO
	Industrial applicability (IA)	Claims 1-16	YES
	industrial application (in 1)	Claims	NO

- 2. Citations and explanations
- (a) The following ISR documents have been considered:
- (1) US 336599
- (2) DE 2753183
- (3) US 3504091
- (4) EP 456198
- (5) JP 56-115739
- (6) US 4125400
- (7) EP 225580
- (8) EP 312313
- (9) US 3377281
- (10) DE 4318210
- (11) AU 16006/88
- (12) 22433/88
- (b) Documents 2,5,6 and 10-12 do not teach or disclose the oils or additives claimed in claims 1,6 and 15 (and appended claims).
- (c)
- (i) Claims 1-5 and 15-16 are not novel and do not involve an inventive step in the light of citations 1,3,4 and 7-9
- (ii) Citations 1 in US column 3 lines 8-25 discloses long chain amines and various oils.
- (iii) Citation 3 in US column 2 lines 44-45, column 2 lines 35-37 and column 2 lines 23-27 discloses sulphonate salts and esters and various oils.
- (iv) Citation 4 at EP page 3 lines 12-15 and 21-25 discloses sulphonates and various oils.
- (v) Citations 7-9 all disclose sulphonates and phenates (citation 7 only discloses both of these) and various oils.
- (vi) The various oils in citations 1,3,4 and 7-9 (or certainly some or most of them) are the same as those of claim 10 and are clearly suitable for use as "agricultural spray oils".

#### Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of : BOX V

d)

- (i) Please note that claims 15 and 16 are both directed to an additive "per se" as the term "and/or" means that either one may be present "alone".
- (ii) In view of (d) (i) above claims 15 and 16 are not novel in the light of the basic compounds of claim 1 and the UV deactivators of claim 6 which are all known "per se" as sulphonates, phenates, amines, benzotriazole UV absorbers, etc. are all well known "per se".
- (e)
  (i) Further to (c) and (d) above please note that the phrases "agricultural spray oil" "additive composition" and "for an agricultural spray oil" in claims 1,6 and 15 (and appended claims) are descriptive only and refer to an "intended" use rather than an "actual" use. Therefore a 'lubricating" oil (as in citations 7-9) would be covered by claims 1,6, etc. as long as it is suitable for use as an agricultural spray oil. See (c) (vi) above.
- (ii) The above matters are explained in PCT/GL/3 Chapter III page 24 paragraph 4.8 and PCT/GL/3 chapter IV page 37 paragraph 7.6.

VI.	Certain documents cit	ed	·			
۱.	Certain published documents (Rule 70.10)					
	Application No. Patent No.	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim		
	US 5439602	8 August 1995	6 July 1994	6 July 1994		
			•			
				9		
	Non-written disclosures		tten disclosure	f written disclosure referring to non-written disclosure (day/month/year)		
		Date of non-writ	tten disclosure	non-written disclosure		
		Date of non-writ	tten disclosure	non-written disclosure		
		Date of non-writ	tten disclosure	non-written disclosure		
		Date of non-writ	tten disclosure	non-written disclosure		
		Date of non-writ	tten disclosure	non-written disclosure		
- 1		Date of non-writ	tten disclosure	non-written disclosure		

;

#### VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

- (a) New page 4 line 29 is not clear as there is no antecedent for "The" free-radical trap or scavenger. Page 4 line 1 refers to a UV deactivator. See also new claim 6(b) which refers to a UV deactivator.
- (b) Page 19 lines 1-2 has repeated the bottom two lines of page 18 and should therefore be deleted.
- (c) Claim 1 is not clear due to the term "sulphonate". Is it a 'metal", sulphonate "salt' or a sulphonate "ester"? Page lines 20,24 and 26 suggest "metal" salts.
- (d) Claim 15 refers to a "base" rather than "a basic compound" as in claim 1. There is therefore no antecedent in claim 1 for the "base" of claim 15 as claim 1 refers to a "basic compound".
- (e) (i) Claim 16 is not clear. Is it claiming the additive "per se" or an oil "containing" the additive?
  - (ii) Claim 16 needs to be be redrafted (See, for example, claim 14).
  - (iii) The term "is" in claim 16 line 2 suggests that the additive may be stored for future use and perhaps several months or even years later it may be added to an oil.
  - (iv) The phrase "is added" suggests an intended future use and therefore claim 16 needs to be redrafted. See, for example, claim 1 line 1 (oil having added thereto...), claim 6 line 1 and claim 14.
  - (v) See also novelty comments (d)(i) and (d)(ii).
- (f) Claim 16 is appended to claim 21 instead of claim 15.

- 17 -

#### CLAIMS:

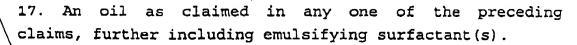
- 1\ An oil for agricultural use having added thereto an oil soluble basic compound.
- 2. An oil as claimed in claim 1, wherein the basic compound is:
  - (≒) \ a sulphonate;
  - (b) \ a phenate;
  - (c) \ a hydroxy containing compound; and/or
  - (d) \an amine.
- 10 3. An oil as claimed in claim 2, wherein the basic compound is an overbased sulphonate or phenate.
  - 4. An oil as claimed in claim 2 or claim 3, wherein the basic compound is a calcium overbased sulphonate.
- 5. An oil as claimed in claim 4, wherein the calcium overbased sulphonate is present in the oil in a range 0.01-5.0 wt% total.
  - 6. An oil as claimed in claim 5, wherein the calcium overbased sulphonate is present in the oil in an amount of about 1.0 wgs total.
- 20 7. An oil for agricultural use having added thereto an oil soluble UV deactivator.
  - 8. An oil as claimed in claim 7 wherein the UV deactivator is:
    - (a) a UV absorber;
- 25 (b) a free-radical trap or scavenger.
  - 9. An oil as claimed in claim 8, wherein the UV absorber is:

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- (i) a benzotriazole compound;
- (ii) an ortho-hydroxy benzophenone compound;
   or
- (iii) a benzoxazole, benztriazole or benzthiazole compound.
- 10. An oil as claimed in claim 9, wherein in (i) the UV absorber is:
- (a)\ TINUVIN 171; or
- (b) \iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-10 4-hydroxyphenyl) propionate.
  - 11. An oil as claimed in claim 10, wherein compound (b) is present in the range of 0.001-0.5 wt% total.
- 12. An oil as claimed in claim 10, wherein compound (a) is present at about 0.005 wt% total; or compound (b) is present at about 0.1 wt% total.
  - 13. An oil as claimed in claim 8, wherein the free-radical trap or scavenger is a metal dithiocarbamate.
  - 14. An oil as claimed in claim 13, wherein the metal dithiocarbamate is zinc diamyldithiocarbamate.
- 20 15. An oil as claimed in any one of the preceding claims, wherein the oil portion is a  $C_{15}$  to  $C_{35}$  light paraffinic or light naphthenic petroleum derived oil.
  - 16. An oil as claimed in claim 15, wherein the light paraffinic or light naphthenic oil is:
    - (a) chemically neutralised;
    - (b) clay treated;
    - (c) solvent refined; or
    - (d) hydro-treated.



- 18. An oil as claimed in claim 17, wherein the surfactant(s) is/are nonionic surfactant(s) and is/are added at about 0.5 wt% to 20.0 wt% total of the oil.
  - 19. An oil for agricultural use including the oil soluble basic compound as defined in any one of claims 1 to 6 and the UV deactivator as defined in any one of claims 7 to 14.
- 20. An additive composition for an oil for agricultural use including a base as defined in any one of claims 1 to 6 and/or a UV deactivator as defined in any one of claims 7 to 14.
- 21. An additive composition as claimed in claim 21, wherein the oil to which the composition is added is as defined in claim 15 or claim 16, and wherein the additive composition optionally includes emulsifying surfactant(s) as defined in claim 17 or claim 18.

DATED this 27th day of March 1996

<u>AUSTRALIAN PETROLEUM PTY LIMITED</u>

By their Patent Attorneys

GRIFFITH HACK & CO.

adda'

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- 3 -

# SUMMARY OF THE INVENTION

In a first aspect, the present invention provides an oil for agricultural use having added thereto an oil soluble basic compound.

By employing an oil soluble base, at least some of any acidic compounds present in or formed in the acid can be neutralised.

Preferably, the basic compound is:

- (a) a sulphonate;
- 10 (b) a phenate;
  - (c) a hydroxy containing compound; and/or
  - (d) an amine.

Thus, a large variety of bases can be added to the oil as appropriate.

In this regard, it is preferred that the basic compound is an overbased sulphonate or phenate, and it is particularly preferred that the basic compound is a calcium overbased sulphonate.

Preferably, the calcium overbased sulphonate is present in the oil in a range 0.01-5 wt% total. It is most preferred that the calcium overbased sulphonate is present in the oil in an amount of about 1.0 wt% total. A metal overbased sulphonate includes an aqueous micelle defined by a plurality of relatively long-hydrocarbon chain molecules having a polar head (ie. sulphonate functionality) and a hydrophobic tail (eg. long chain alkyl, and an excess amount of metal base, eg. calcium carbonate in the micelle. (A depiction of an overbased sulphonate is shown in Figure 5). Metals other than calcium can also be used in the sulphonate or phenate (eg. magnesium overbased sulphonates).

As described above, exposure of a PSO to UV radiation brings about photo-degradation of the PSO (ie. through the photo-oxidation thereof) into p roxides,

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acids, esters, plymers etc, thus increasing the phytotoxicity of the PSO.

In a second aspect, the present invention provides an oil for agricultural use having added thereto an oil soluble UV deactivator.

Photo-oxidation can thus be prevented or ameliorated, or alternatively any photo-oxidation products (eg. peroxide free-radicals) can be scavenged and/or trapped.

Preferably, the UV deactivator is:

10 (a) a UV absorber;

(b) a free-radical trap or scavenger.

The UV absorber absorbs UV radiation and thus tends to prevent photo-oxidation, whereas the free-radical trap or scavenger neutralises any free-radicals produced during photo-oxidation (eg. peroxides).

Preferably, the UV absorber is:

- (i) a benzotriazole compound;
- (i) an ortho-hydroxy benzophenone compound; or
- 20 (iii) a benzoxazole, benztriazole or benzthiazole compound.

In this regard, the UV absorber is preferably TINUVIN 171, pref. at 0.005%. (Trade mark of Ciba Geigy).

Alternatively, the UV absorber can be iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl) propionate. (A commercially available form of this compound is known as TINUVIN 384 (Trade Mark of Ciba Geigy Limited. TINUVIN 384 is a liquid UV absorber of the hydroxyphenyl benztriazole class. It has high thermal stability and permanence.

Preferably, the iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl) propionate is present in the range of 0.001-0.5 wt% total of the oil, most preferably at about 0.01 wt% total of the oil.

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preferably, the free-radical trap or scavenger is a metal dithiocarbamate. In this regard it is preferred that the metal dithiocarbamate is zinc diamyldithiocarbamate.

A preferred oil for use as a PSO is a refined light oil ( $C_{15}$  to  $C_{35}$  length of hydrocarbon chain). In particular, it is preferred that the oil portion of the PSO is a  $C_{15}$  to  $C_{35}$  light paraffinic or light naphthenic petroleum derived oil.

10 Preferably, the light paraffinic or light naphthenic oil is:

- (a) chemically neutralised;
- (b) clay treated;
- (c) solvent refined; or
- 15 (d) hydro-treated.

Physical properties of such oils are shown in Tables 2 and 3.

Surfactants are typically added to PSO's to enable the oil to be dispersed in water for subsequent spraying. Typical surfactants include nonionic surfactants. The nonionic surfactants can be added in the range of 0.5 wt% to 20 wt%.

In a most preferred spray oil formulation, a refined light oil can include 0.5 - 20 wt% nonionic surfactant, 1.0 wt% calcium overbased sulphonate and 0.005 wt% benztriazole compound. Thus, preferred formulations may include both an oil soluble basic compound and a UV deactivator.

In a further aspect of the present invention an additive composition for an oil for agricultural use is provided which can include a base (as defined above), and/or a UV deactivator (as defined above).

This additive composition can also include emulsifying surfactant(s) (as defined above). Such an additive composition can be provided separately from the oil (eg. PSO) and can be added to the oil in situ (eg.

## **PATENT COOPERATION TREAT**

	From the INTERNATIONAL BUREAU					
PCT	То:					
NOTIFICATION OF THE RECORDING OF A CHANGE  (PCT Rule 92bis.1 and Administrative Instructions, Section 422)  Date of mailing (day/month/year) 18 November 1996 (18.11.96)	GRIFFITH HACK & CO. G.P.O. Box 4164 Sydney, NSW 2001 AUSTRALIE					
Applicant's or agent's file reference P05319EI:RPW	IMPORTANT NOTIFICATION					
International application No. PCT/AU96/00189	International filing date (day/month/year) 02 April 1996 (02.04.96)					
The following indications appeared on record concerning:      The applicant						
Name and Address  AUSTRALIAN PETROLEUM PTY. LIMITED Level 14 167-187 Kent Street Sydney, NSW 2000 Australia	State of Nationality  Telephone No.  Facsimile No.  Teleprinter No.					
The International Bureau hereby notifies the applicant that the the person the name X the add						
Name and Address  AUSTRALIAN PETROLEUM PTY. LIMITED Level 22 MLC Centre 19-29 Martin Place Sydney, NSW 2000 Australia	State of Nationality State of Residence  Telephone No.  Facsimile No.  Teleprinter No.					
3. Further observations, if necessary:						
4. A copy of this notification has been sent to:    X   the receiving Office						
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740 14 35	Authorized officer  Catherine Massetti  Telephone No.: (41-22) 730 91 11					

## FATENT COOPERATION TREAT

	From the INTERNATIONAL BUREAU			
PCT	То:			
NOTIFICATION OF ELECTION	United States Patent and Trademark			
(PCT Rule 61.2)	Office (Box PCT)			
	Crystal Plaza 2 Washington, DC 20231			
	ETATS-UNIS D'AMERIQUE			
Date of mailing (day/month/year) 22 November 1996 (22.11.96)	in its capacity as elected Office			
International application No.	Applicant's or agent's file reference P05319E1:RPW			
PCT/AU96/00189	Priority date (day/month/year)			
International filing date (day/month/year) 02 April 1996 (02.04.96)	05 April 1995 (05.04.95)			
Applicant				
HODGKINSON, Mark				
1. The designated Office is hereby notified of its election made:    X   in the demand filed with the International Preliminary Examining Authority on:   30 October 1996 (30.10.96)   in a notice effecting later election filed with the International Bureau on:   2. The election   X   was   was not   was not   was not   was not   was not   was not   was 2.2(b).				

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35 Authorized officer

Catherine Massetti

Telephone No.: (41-22) 730.91.11

Form PCT/IB/331 (July 1992)

1304907